



Effect of water washing on the thermal behavior of rice straw



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ABSTRACT

Rice straw can be used as a renewable fuel for heat and power generation. It is a viable mean of replacing fossil fuels and preventing pollution caused by open burning, especially in the areas where this residual biomass is generated. Nevertheless, the thermal conversion of rice straw can cause some operating problems such as slag formation, which negatively affects thermal conversion systems. So, the main objective of this research is studying the combustion behavior of rice straw samples collected from various regions by applying thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In addition, the thermal behavior of ashes from rice straw was also analyzed in order to detect their melting points, and ash sintering was detected at different temperatures within the range between 550 and 1000 °C. Since washing rice straw with water could reduce the content of undesirable inorganic compounds related to the ash fusibility, samples of washed rice straw were analyzed under combustion conditions to investigate its differences regarding the thermal behavior of rice straw. The results showed that rice straw washing led to a significant improvement in its thermal behavior, since it reduced the ash contents and sintering formation.

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1. Introduction

Biomass materials with high energy potential include agricultural residues and all of the agricultural residues are biological forms of renewable energy, rice straw is considered to be the most important of such residues and represents one of the major by-products from rice production process in most rice producing countries (Abou-Sekkina et al., 2010; Said et al., 2013; Werther et al., 2000). The rice collection harvest generates large amounts of straw, for each ton of grain harvested, about 1.35 tons of rice straw remain in the field (Kadam et al., 2000) making up approximately 50% of the dry weight of rice plants, with a significant variation of 40–60% depending on the crop and agricultural method. The annual production of rice straw is about 731 million tons which is distributed in Africa, Asia, Europe, America and Oceania as 20.9, 667.6, 3.9, 37.2 and 1.7 million tons, respectively (Balat et al., 2008; Sarkar et al., 2012).

During the rice harvest, the elimination of rice straw is frequently carried out by farmers by burning it in the fields because of the difficulty and high cost of removing it and because of its null use (Abril et al., 2009); the justification for this practice is the reincorporation

of part of the necessary nutrients for the crop (N, P, K and amorphous silica) (Datnoff et al., 1997). However, open burning after grain harvest results in emissions to air that have a deleterious effect on air quality and human health (Suramaythangkoor and Gheewala, 2010); these emissions show high concentrations of pollutants in form of particles (PM_{2.5} and PM₁₀), CO_x, hydrocarbons, NO_x, SO₂, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), polychlorated compounds, dioxins and furans, with the corresponding affection to the environment and to human health (Abril et al., 2009; EEA, 2007). There are other elimination options such as crushing and mixing it with the soil, or removing it for its use. Since the alternative of burying the straw generates between 2.5 and 4.5 times more methane than burning it, this practice is not recommendable either (Fitzgerald et al., 2000); moreover, the abandoned rice straws in the field sometimes may flow into the drainage during the rainy season, causing an obstruction of the drainage, or providing the place for the propagation of the bacteria (Chou et al., 2009).

Rice straw as agricultural waste biomass could be a source of alternative energy that therefore substitutes fossil energy for reducing greenhouse gas emissions as well as avoids the local pollution problems from open burning (Suramaythangkoor and Gheewala, 2008). Because of the high price of crude oil, attention has been focused on rice straw as a potential renewable energy source (Lee et al., 2005); however it has not yet been commercially used as a feedstock for heat and energy because of insufficient

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incentives or benefit for farmers to collect rice straw instead of field burning (Kargbo et al., 2009). Generating electricity by burning straw directly not only saves energy, protects the environment, and reduces field-burning pollution, but also increases the income of farmers (Zhaosheng et al., 2008). Due to low bulk density, rice straw is difficult to handle, transport, store, and utilize in its original form. It should be processed by densification techniques such as pelletizing or briquetting. The densified rice straw can be easily handled and can reduce the costs of transportation, handling and storage, moreover, the densification process also provides potential storage for off-season utilization (Ewida et al., 2006; Gilbert et al., 2009; Kaliyan and Morey, 2009).

Rice straw can also be converted into energy via processes including direct and indirect techniques. The direct techniques include standalone burning and co-firing it with other fuels, and the indirect technique includes gasification, pyrolysis, anaerobic digestion, thermo-chemical conversion and liquid fuel production, where these products can then be burned (Ewida et al., 2006). Burning rice straw either with other fuel or stand-alone has the advantage of high energy conversion efficiency compared with indirect techniques. On the other hand, it suffers from some technical limitations and causes operating problems in thermal conversion systems. These problems include high ash content, sintering, fouling, slag formation, and corrosion problems. This has the drawback of retarding the rate of heat transfer as a result of low thermal conductivity and high reflectivity (Jenkins et al., 1996; Zygarlicke et al., 2000). Sinters and slags problems are mainly related to a high relative content of alkaline compounds in straw ashes, during combustion in the furnace, K compounds evaporate to form KCl and K₂SO₄. These compounds and other mixtures of ash compounds have low melting point temperatures; straw ash melting point is 1000 °C or even less (Bryers, 1996; Picco, 2010). The high contents of salts, alkali oxides attributed to the use of fertilizers in agricultural farms, and low melting points can lead to various problems during combustion process (Bapat et al., 1997; Grubor et al., 1995).

For using rice straw to generate energy efficiently and obtain products with high added value, it is necessary to develop an industry of collection, transport and storage as well as solve the difficulties caused by the high content of silica (Abril et al., 2009) and other components. Using additives for rice straw such as kaolin or blending rice straw with other fuels such as coal may be suggested solutions to enhance combustion efficiency of boilers and to control fouling and slag formation (Picco, 2010). However, practical experiences with co-combustion of rice straw show a certain increase of slagging tendency in high temperature part of the boiler, comparing with coal combustion (Pronobis, 2005), meanwhile, co-combustion of rice straw with wood based fuel may be beneficial and may reduce fouling (Thy et al., 2004). Leaching rice straw with water is a possible way of reducing the content of the undesirable compounds which cause fouling and slag formation (Bakker et al., 2002; Jenkins et al., 1996).

The main objective of this research was to study the thermal behavior at different temperatures of washed and unwashed rice straw from different regions in Spain (Andalusia, Murcia and Valencia) and Egypt (El Sharkia province). The combustion behavior of the straw was studied using thermal analysis (TGA and DSC) as a complimentary method provides useful and valuable information about the nature and composition of the organic wastes, moreover, it is widely used to study the mechanisms of the thermal decomposition and combustion of biomass (Fernández et al., 2012; Zhaosheng et al., 2008). Furthermore, ash melting points, ash content, and ash sintering were investigated at different temperatures within the range between 550 and 1000 °C.

2. Material and methods

2.1. Sampling

The rice straw samples were collected from different provinces in Spain (Andalusia, Murcia, and Valencia), and Egypt (El Sharkia province). According to Deng et al. (2013), water washing appears to be a more controllable manner than natural rain washing and washing with tap water and distilled water makes no difference to element removal, washing the straw samples with tap water is used in this study as a simple and an effective method to remove a large part of troublesome elements from biomass fuels.

The straw samples were cut to 10 cm then washed with flushed tap water and dried at 105 °C to a constant weight. Elemental analysis for the dried washed and unwashed straw samples was performed according to UNE-EN 15104: 2011. Before the application of the experimental methods, the particle size for the unwashed and the dried washed samples was reduced to less than 0.5 mm to ensure the heat transfer rate within the kinetic regime of decomposition (Rath et al., 2002). Moreover, the initial mass of the sample was between 2–5 mg for the ash and between 6–8 mg for the rice straw to avoid any possible effect on mass and heat transfer during the process of biomass decomposition (Blasi et al., 2001; Calvo et al., 2004).

2.2. Analytical procedures

2.2.1. TGA and DSC

The TGA and DSC of the samples were performed using a SHIMADZU TGA-50H thermo analyzer in an oxidative atmosphere. The samples are heated from 30 to 1000 °C at heating rate of 5 °C/min for the ash and 10 °C/min for the rice straw, to maintain an oxidative atmosphere for thermal decomposition of the particles and this heating rate is generally considered capable of ensuring that there is no temperature gap between the sample and its surroundings, moreover, the low heating rate makes the chemical kinetic properties of the biomass sample clearer (Bilbao et al., 1997; Deng et al., 2013; Liu et al., 2002). According to Calvo et al. (2004) and Saddawi et al. (2012), an air atmosphere was passed continuously at a flow rate of 100 mL/min for the rice straw and 50 mL/min for the ash; moreover, higher flow rate was applied and did not give uniform and expressed relation for the thermograms. The oxygen in the air atmosphere enhances the decomposition of the material at low temperatures, and when the temperature becomes sufficiently high, oxygen is likely to cause the combustion of the char residue generated in the early stages of solid decomposition (Liu et al., 2002). The analysis for each sample was repeated to ensure that it follows the same trace for the same conditions.

2.2.2. Ash and volatile matter (VM) content

Ash contents of unwashed (U) and washed (W) rice straw samples were determined by igniting grinded straw samples in muffle furnace at 550 °C according to UNE-EN 14775:2010 and VM was determined at 900 °C according to UNE-EN 15148:2010. Three measurement series per sample were obtained and the average value was calculated.

Elemental composition of the ash obtained at 550 °C for the washed and unwashed straw samples was analyzed through X-ray Fluorescence according to UNE-EN 15290:2011.

2.2.3. Heating value

Higher heating value (HHV) at constant volume was determined by adiabatic bomb calorimeter according to UNE-EN

14918:2011. Three measurement series per sample were obtained and the average value was calculated.

2.2.4. Melting point, sintering and slagging tendencies

Melting points were detected from DSC thermograms of the different rice straw ash samples. The sintering of the unwashed and washed rice straw samples was detected by combusting the samples in a muffle furnace and observing the appearance at different temperatures (550–1000 °C) (Bakker et al., 2002; Jenkins et al., 1996). The prediction of slagging or fouling tendencies of the washed and unwashed straw samples has been determined using the alkali index that expresses the quantity of alkali oxide in the biomass per unit of fuel energy. It has been computed according to Eq. (1) where I is the alkali index, expressed as kg alkali/GJ or lb alkali MMBtu⁻¹, Q is the heating value (GJ/kg), Y_f is the mass fraction (dimensionless) of ash, Y_{K_2O} and Y_{Na_2O} are the mass fractions (dimensionless) of K_2O and Na_2O in the ash (Jenkins et al., 1998; Skrifvars et al., 2005). Miles et al. (1995) suggested that above 0.17 kg alkali/GJ (0.4 lb alkali MMBtu⁻¹) fouling is probable, and above 0.34 kg/GJ (0.8 lb MMBtu⁻¹), fouling is virtually certain to occur.

$$I = (1/Q)Y_f(Y_{K_2O} + Y_{Na_2O}) \quad (1)$$

3. Results and discussion

3.1. Straw composition and ash content

The harvesting time, soil, cultivation and storage conditions of the rice straw, such as its exposure to rain washing and soil contamination, are factors that may affect its properties (Bakker et al., 2002; Jenkins et al., 1996; Pronobis, 2005).

The composition of different straw samples is shown in Table 1. Carbon contents in the different samples ranged between 39.01% and 41.24%, hydrogen content were between 6.49% and 6.99% and nitrogen content in the range of 0.4% and 1.23%. Soil contamination may be high and may result in an increase in the percentage of some elements for the unwashed straw and due to washing this percentage decreases but also may increase for other main constituent components of the straw such as C and H, where the removing of the other surface elements by water washing result in an increase of their contents as a percentage of the whole straw. After washing the straw, almost all the washed straw samples showed an increase in carbon, hydrogen and VM content with ratio reached to 16.45%, 8.47% and 3.42%, respectively, in Valencia straw. A decrease in nitrogen content for most of the samples has been detected and reached to 59.38% in Egypt straw, see Table 2. Similar results were found with other authors (Bakker et al., 2002; Deng et al., 2013; Jenkins et al., 1996; Lee et al., 2005; Saddawi et al., 2012).

Ash contents of the washed and unwashed straw samples are indicated in Table 1. Valencia straw recorded the highest ash

Table 2

The variation in the parameters due to straw washing.

Parameter	Egypt	Murcia	Valencia	Andalusia
Ash content	−17.06	−10.66	−15.80	−19.77
HHV	+5.29	+1.84	+7.82	+7.89
VM	+1.81	+0.42	+3.42	+0.97
C	+3.59	–	+16.45	+3.83
H	+2.58	−1.62	+8.47	+2.72
N	−59.38	−10.00	−32.52	+23.81
Alkali index	−43.46	−55.43	−60.77	−63.24

–: No variation has been detected.

The negative values indicate reduction percentage in the parameter value due to washing.

The positive values indicate increasing percentage in the parameter value due to washing.

content followed by Egypt, Murcia and Andalusia straw. Reduction in ash contents has been observed for all the samples by washing the straw, however the reduction percentage in ash content due to washing depended on the type of sample; it reached from 10.66% in the case of sample from Murcia straw to about 19.77% in Andalusia straw, see Table 2. Ash content reduction was due to that washing the straw extracts large amounts of alkali metals, chlorine, in addition to variable amounts of sulfur, phosphorus and other elements caused by contamination of the straw with soil (Bakker et al., 2002; Deng et al., 2013; Jenkins et al., 1996; Kargbo et al., 2009; Skrifvars et al., 2005), see Table 3. This table shows that the washing was very efficient in chlorine removal and was significant in the other elements; the chlorine, magnesium and phosphorous removal ratios reached to about 87%, 39% and 35%, respectively in Valencia straw. About 60% sodium and sulfur removal were recorded in Andalusia and Egypt straw, respectively. Potassium removal ratio reached about 50% in Murcia, Valencia and Andalusia straw, where the potassium can be dissolved very well in water (Lee et al., 2005).

3.2. TGA and DSC for the straw samples

TGA and DSC thermograms in an air atmosphere for the different unwashed straw samples have been detected to determine the thermal nature as shown in Fig. 1. These thermograms showed slight difference for the different straw samples. TGA curve indicated the mass loss of the sample. It initially decreases below 100 °C because of drying and loss of the moisture that the samples contained owing to the hygroscopic nature of rice straw and there may be also loss of very light volatiles (Calvo et al., 2004; Singh, 1996). After 200 °C, straw devolatilization begins and high loss in the weight occurs due to decomposition and the emission of volatiles from cellulose and hemicelluloses, also small amounts of volatiles from the lignin component may also given off (Calvo et al., 2004; Koufopoulos and Maschio, 1989; Sun et al., 2002). After 300 °C, the weight loss is corresponding to lignin decomposition

Table 1

Analysis data of unwashed straw samples.

Parameter	Egypt			Murcia			Valencia			Andalusia		
	Average	Min	Max	Average	Min	Max	Average	Min	Max	Average	Min	Max
Ash content (%)	16.81	16.46	17.04	15.52	15.48	15.60	18.66	18.46	18.90	13.25	13.19	13.32
HHV (MJ/kg)	14.17	13.81	14.43	14.67	14.36	14.94	14.06	13.82	14.22	14.96	14.93	14.98
VM (%)	85.19	84.94	85.58	86.19	86.08	86.27	81.93	81.76	82.12	89.04	88.92	89.15
C ^a (%)	39.01			40.64			37.74			41.24		
H ^a (%)	6.59			6.80			6.49			6.99		
N ^a (%)	0.64			0.40			1.23			0.63		
Alkali index ^a (kg alkali/GJ)	1.91			1.75			2.09			1.85		

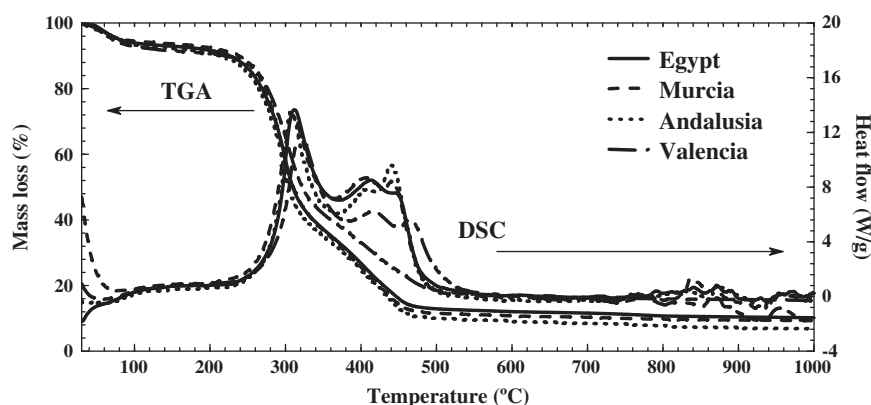
^a The variations of this parameter were imperceptible (about 0.01% in some of the samples tested), so the maximum and minimum values would fit in with the average value.

Table 3

Percentage of inorganic elements in ash and removal ratio due to washing.

Parameter ^a	Egypt		Murcia		Valencia		Andalusia	
	(%) Ash	% Removal	(%) Ash	% Removal	(%) Ash	% Removal	(%) Ash	% Removal
Na	2.30	35.65	0.73	40.08	1.61	52.86	2.02	59.95
K	10.80	26.14	12.92	49.48	11.25	49.38	15.06	49.09
Mg	1.35	21.98	1.36	–	2.93	38.80	2.03	17.97
P	0.30	7.80	0.42	–	0.78	34.83	0.45	–
S	0.50	59.44	0.69	30.26	1.43	55.24	0.82	25.46
Cl	5.40	59.04	4.18	80.82	4.70	86.96	7.54	82.90

–: No removal has been detected.

^a The variations of these parameters were imperceptible (about 0.01% in some of the samples tested), so the maximum and minimum values would fit in with the average value.**Fig. 1.** TGA and DSC thermograms of the different straw samples.

and the decomposition rate becomes very low after 460 °C and becomes negligible at around 600 °C, similar results found by Jung et al. (2008). The maximum mass loss has been occurred in the range between 200 and 500 °C for the different straw samples. DSC thermograms show that the overall thermal degradation of rice straw is an exothermic process and the large exothermic peaks were observed at around 300 °C, which is attributed to the decomposition of hemicelluloses and cellulose (Chakraverty et al., 1987; Sun et al., 2002). Andalusia straw recorded the highest mass loss rate and lowest char residue in TGA profile and the highest exothermic peak in DSC profile compared to the others. It may be related to its lowest ash content and highest volatiles among the different straw samples (Table 1). In the other hand, Valencia straw recorded the lowest mass loss rate, highest char residue and the lowest exothermic peak, meanwhile, the TGA and DSC curves for Egypt and Murcia straw are nearly close.

As one example of the different rice straws, Fig. 2 shows TGA and DSC thermograms of washed and unwashed Andalusian rice straw. TGA profiles showed lower degradation residues, namely char, in the washed straw compared to the unwashed straw. This may be due to the lower metals content in the washed straw that acts as a catalyst in the formation of char (Raveendran et al., 1995). In contrast, the DSC profile for the washed straw recorded higher exothermic peak than the unwashed straw. This may be due to increase volatiles content in the washed straw (Table 2) compared to the unwashed straw (Lee et al., 2005).

3.3. Heating value

The HHV of the unwashed straw reached values between 14.06 and 14.96 MJ/kg (Table 1), similar to other studies (Bakker et al., 2002; Calvo et al., 2004; Deng et al., 2013; Jenkins et al., 1998; Jung et al., 2008; Skrifvars et al., 2005), and differences between the samples has not been detected.

After washing, the heating value increases with a percentage varied from 1.84% in the case of the sample from Murcia to 7.89% in Andalusia straw. The increase in HHV may be correlated to the decrease in the ash content of the washed straws (Jenkins et al., 1996). Table 2 shows that the highest reduction in ash content with the highest increase in HHV were occurred in Andalusia straw, whenever, Murcia straw recorded the lowest ash reduction and lowest increase in HHV due to washing. Moreover, the compositional changes after washing such as the increase of carbon values of the washed straw, as shown in Table 2, lead to modest increases in heating value (Bakker et al., 2002).

3.4. Melting point, sintering and slagging tendencies

3.4.1. Ash melting point

Since the fuel ash consists of a mixture of different inorganic compounds, the ash has no well defined melting point and the melting process takes place over a wide temperature range starting with the initial deformation temperature (where sintering begins), continuing with the hemisphere temperature and ending with the flow temperature (Picco, 2010; Saddawi et al., 2012). The DSC curves for the different unwashed rice straw ashes were detected in order to ascertain the melting point. Fig. 3 shows the DSC curves for the different rice straw ash samples. It was possible to represent the melting points as maximum of the endothermic peaks of the DSC traces (Buzarovska et al., 2008). The maximum endothermic peaks for the different samples were in the range between 700 and 800 °C.

3.4.2. Sintering and slagging tendencies

The appearance of unwashed and washed straw samples was observed by combustion at different temperature (550–1000 °C). The unwashed straw samples showed light ash sintering at temperature 700–800 °C, Fig. 4b, whereas severely sintering and

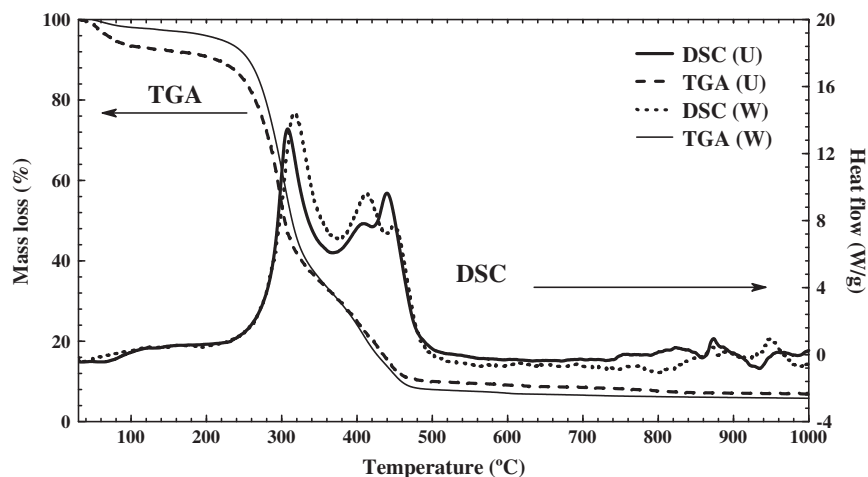


Fig. 2. TGA and DSC thermograms of washed and unwashed Andalusia straw.

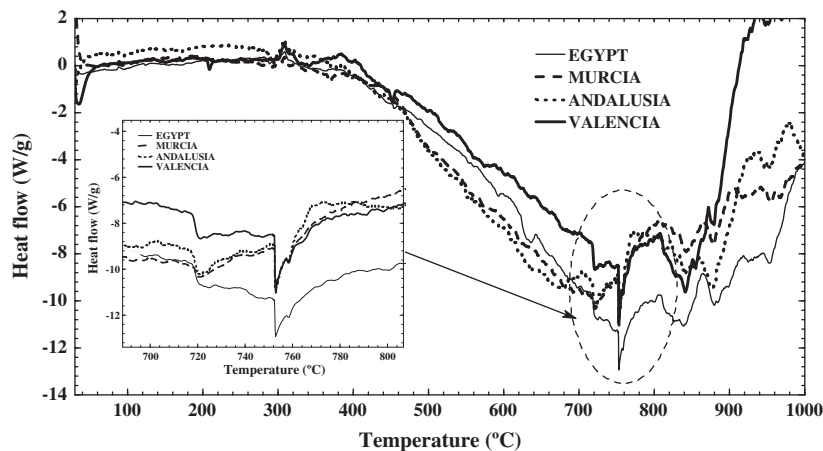


Fig. 3. DSC thermograms for the different straw ash samples.

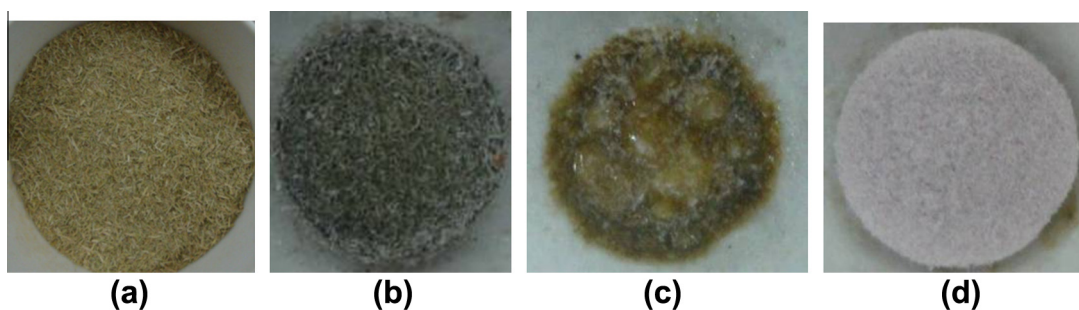


Fig. 4. Rice straw: (a) before combustion; (b) unwashed straw at (700–800 °C); (c) unwashed straw at (900–1000 °C); (d) washed straw at (900–1000 °C).

crystallized appearance was observed at 900–1000 °C, as shown in Fig. 4c. After washing, the washed straw samples were combusted at the same temperature range and the ash sintering of the unwashed samples was not observed in the washed samples, see Fig. 4d. Bakker et al. (2002) studied the evaluation of the ash from the muffle furnace experiments and revealed that the ash from rice straw severely sintered at 900 °C, while leached straw exhibited only light sintering at 1000 °C. Jenkins et al. (1996) found that the ash, which sintered at temperatures of 900–1000 °C for rice straw, was not observed in well washed samples though some sintering occurred at temperatures higher than 1100 °C.

Table 1 lists the alkali index values for the unwashed rice straw which are computed according to Eq. (1). Although all alkali index values exceed the probable value of 0.17 kg alkali/GJ as well as the critical value of 0.34 kg/GJ, which indicates that the samples will slag or foul, an improvement in alkali index values was observed for the washed samples, especially for Andalusian straw, for which the ratio improved by approximately 63.24%, see Table 2.

Sinters and slags of rice straw ash are related to the presence of potassium, chlorine, and silicon in the straw and mainly related to the high relative content of alkaline compounds in straw ashes (Baxter et al., 1998; Peng et al., 2009; Picco, 2010; Werther et al.,

2000). Washing rice straw with water is reducing the content of these undesirable compounds because it extracts large amounts of chlorine and alkali metals, especially potassium, which can be dissolved very well in water. Therefore, it leads to significant changes in inorganic composition and substantially improves combustion behavior (Bakker et al., 2002; Jenkins et al., 1996; Lee et al., 2005).

4. Conclusions

Rice straw could be used as a renewable fuel for heat and power generation, replacing fossil fuels and preventing pollution from rice straw open burning. Thermal conversion of rice straw to energy is attractive option but it causes operating problems that affect thermal conversion systems such as sinter and slag formation due to the presence of potassium, chlorine and silicon in the straw. Washing rice straw with water is a feasible option to reduce the content of troublesome compounds.

Significant improvement in the thermal behavior and reduction in the ash contents, chlorine, alkali metals, and sintering formation were observed in the washed straw in comparison to the unwashed straw. After washing, chlorine and potassium removal ratio reached to about 87% and 50%, respectively. Reduction in ash content and increasing in HHV reached to about 19.77% and 7.89%, respectively. Ash melting point for the different straw samples was in the range between 700 and 800 °C. Light ash sintering was observed for the unwashed straw samples at 700–800 °C and strongly sintering at 900–1000 °C. Ash sintering of the washed samples was not observed for the washed samples at the same temperature range. Moreover, improvement in the alkali index value was observed for the washed samples, the ratio improved by approximately 63.2.

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